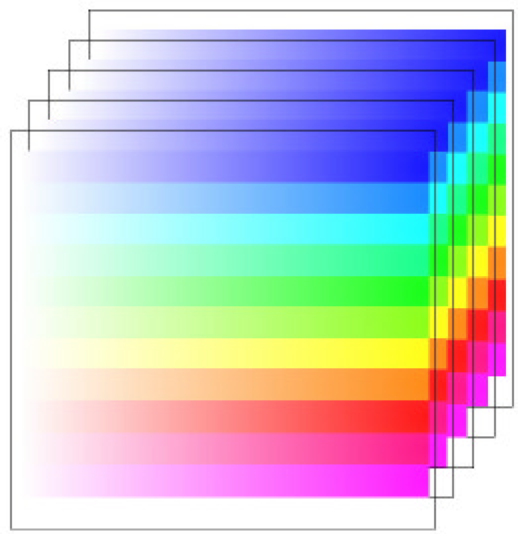
Combinatorial Tools for Inorganic Thin Films



NIST CENTENNIAL 1901-2001

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National Institute of Standards and Technology
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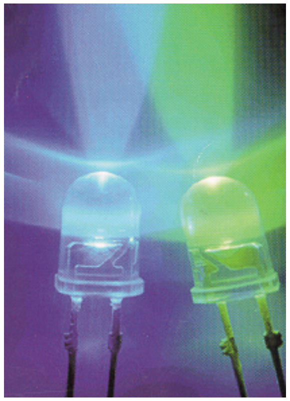
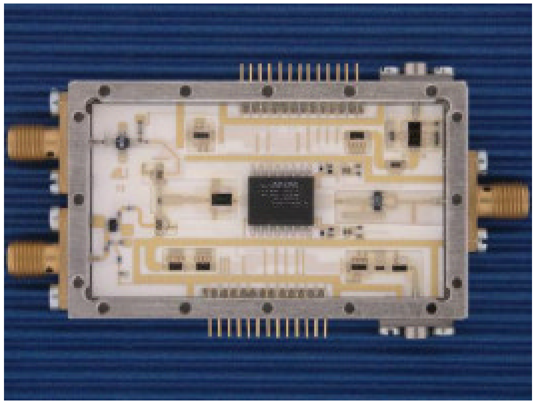
Introduction
Applications of Inorganic Thin Films



optoelectronics



electronics

magnetics

photonics

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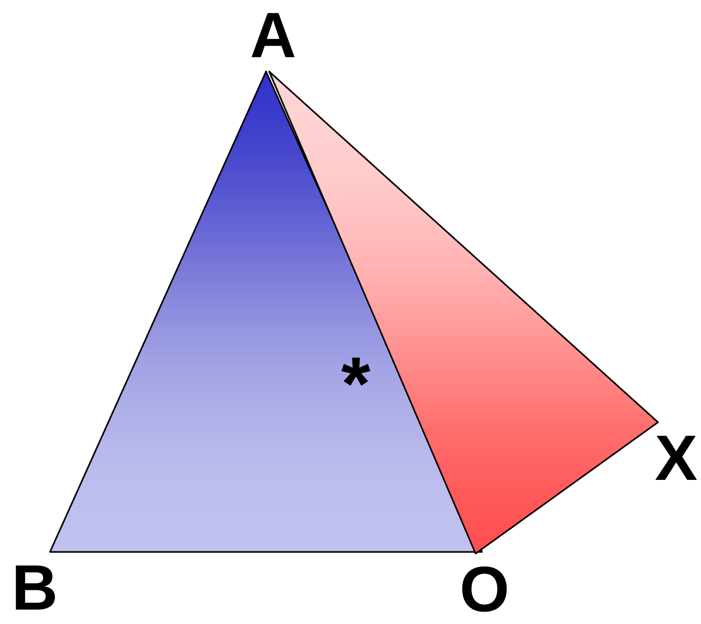
Introduction
Multicomponent Inorganic Systems

- Composed of 3 or more elements
- Properties depend on composition and structure
- Search composition space to:
    - optimize specific property
    - discover new materials
- Explore multiparameter processing space to:
    - optimize structure
    - optimize specific property



Quaternary composition space A- B-O-X

Introduction
Combinatorial Studies of Inorganic Films

Material class	Investigators
Superconductors	Hanak (1970); Xiang (1995)
Magnetoresistors	Briceno (1995)
Phosphors	Sun (1997); Danielson (1997)
Dielectric oxides	Chang (1998), van Dover (1998)
Ferroelectric superlattices	Koinuma (1999)
Semiconductors	Matsumoto (1999)
Optical phase change	Cremer (2001)

Introduction
Objective of our Work

Develop combinatorial tools that are applicable to a broad range of inorganic materials:

- ***Library fabrication***

  Pulsed laser deposition: dual-beam, dual-target

- ***Property assays***

  Thickness & refractive index mapping by spatially-resolved spectroscopic reflectometry

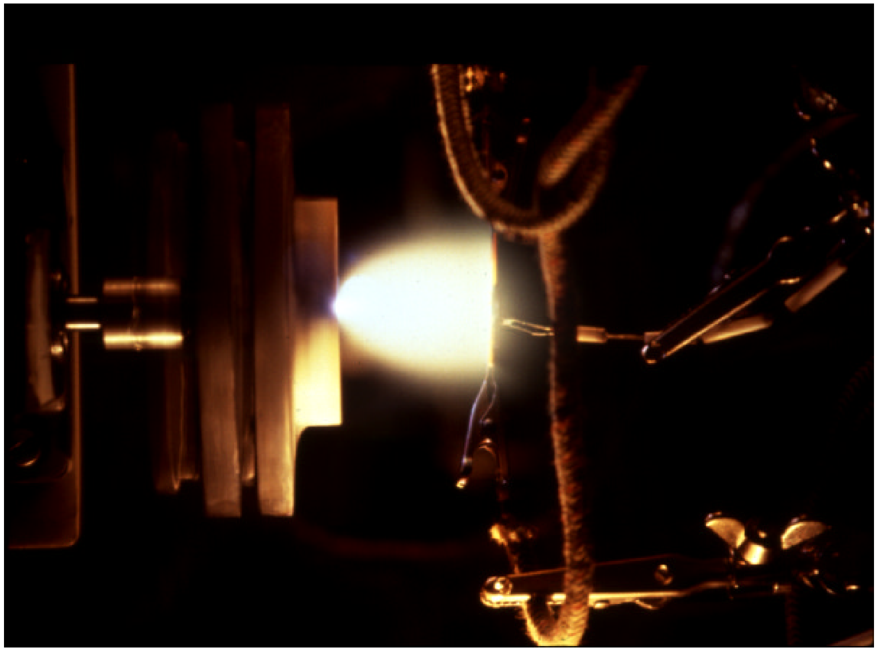
- ***Structural evaluation (preliminary)***

  Phase evolution measurements by x-ray diffraction and spectroscopic reflectometry

Library Fabrication
PLD as a Rapid Prototyping Tool

Advantages:

- Complex target compositions are possible
- Congruent vaporization leads to stoichiometric material transfer
- High energy process
- Higher deposition rates
- Lower substrate temperatures



Laser plume from a single target

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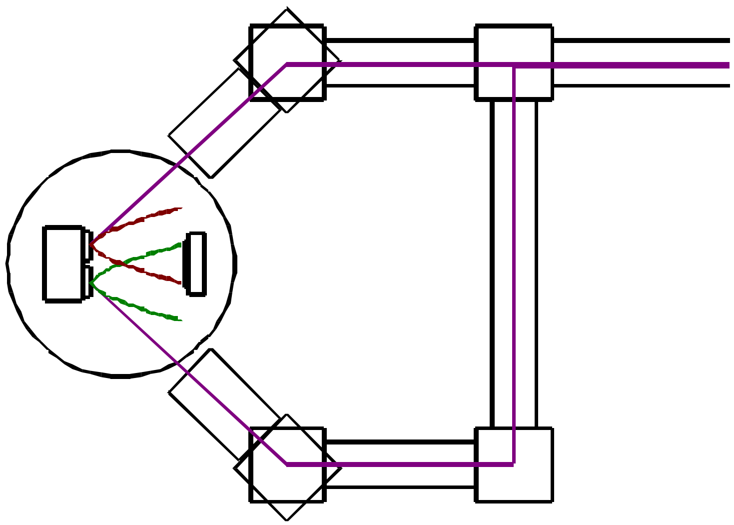
Pulsed Laser Deposition
Dual Beam Design



- *Dual Beam Delivery System*
  - **Adjustable beam dividing mirror apportions the laser energy to the two targets.**
  - **Independent adjustment of focus to control spot size on targets.**
- *Deposition Chamber*
  - **Oil-less pumping and controllable buffer gas pressure.**
  - **Computer controlled heater.**
- *Dual Target System*
  - **Targets rotate and raster in two dimensions relative to laser impact points.**
  - **Utilizes whole target and reduces particulates.**

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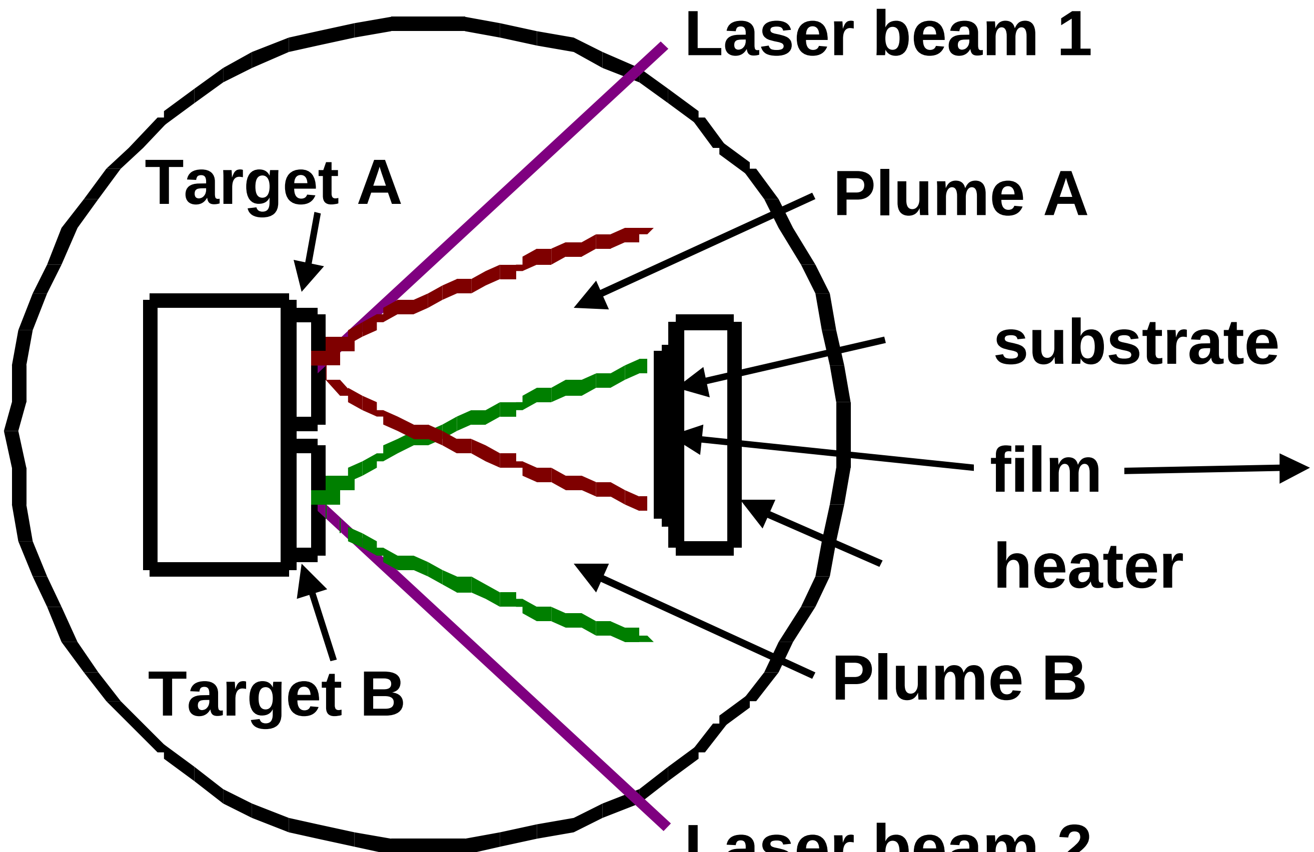
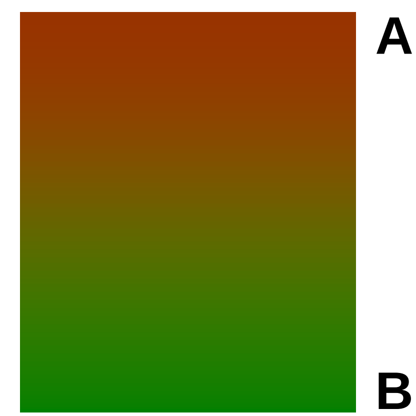
Pulsed Laser Deposition
Co-deposition from Two Targets





Compositionally graded film

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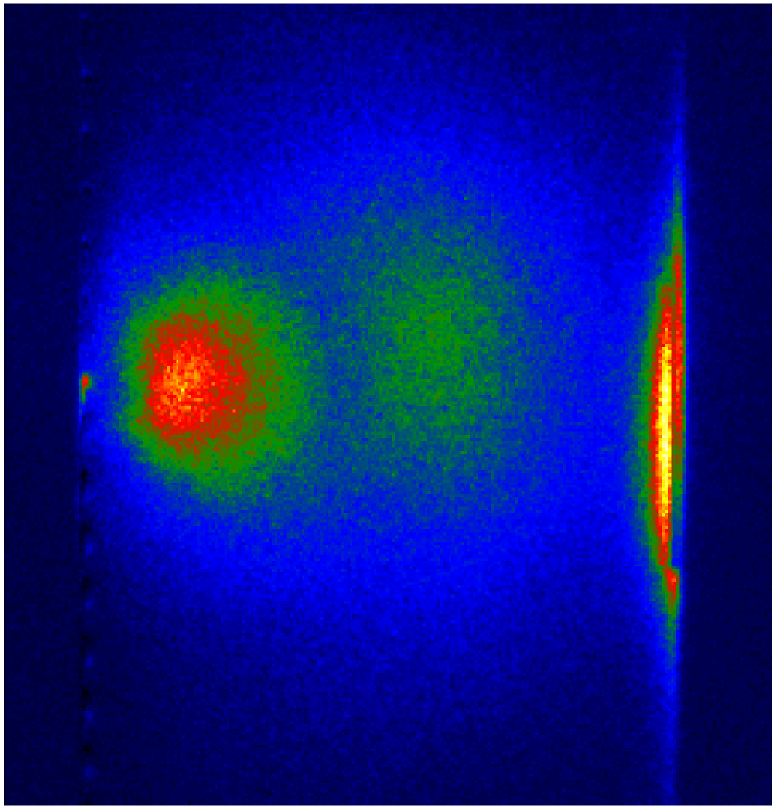
Pulsed Laser Deposition
In-Situ Process Monitoring

- **High speed ICCD camera for imaging laser generated plumes:**
  5 ns resolution
  1 cm field of view
  200-900 nm coverage

- **Dual crystal deposition rate monitor**

- **Adjustable parameters: *laser spot size, energy, target spacing***

- **Fine-tune parameters to get films of a particular composition spread or thickness distribution**



False color ICCD UV image of BT plume at ~1ìs after laser pulse (20 ns exp., 3 cm target to substrate)

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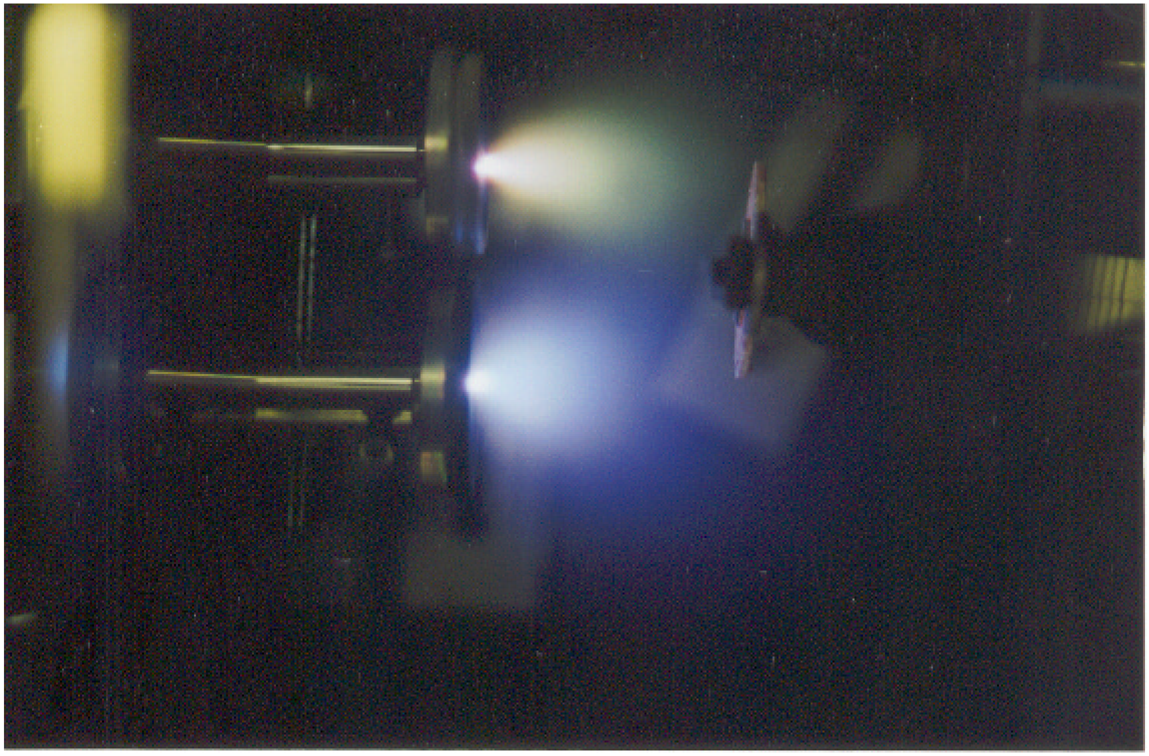
Pulsed Laser Deposition
Plume Imaging



Target - heater distance 3 cm

$BaTiO_3$ - yellow $SrTiO_3$ - blue

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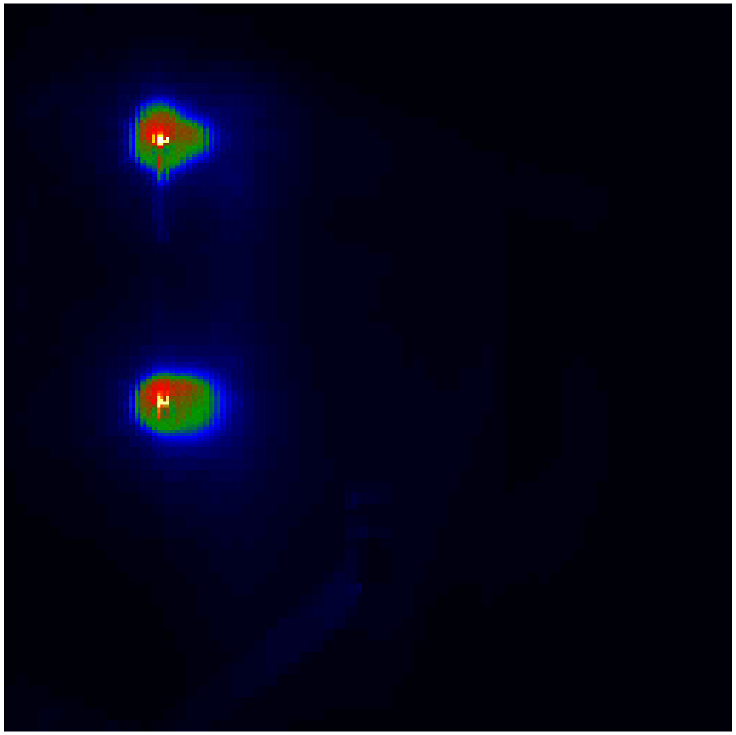
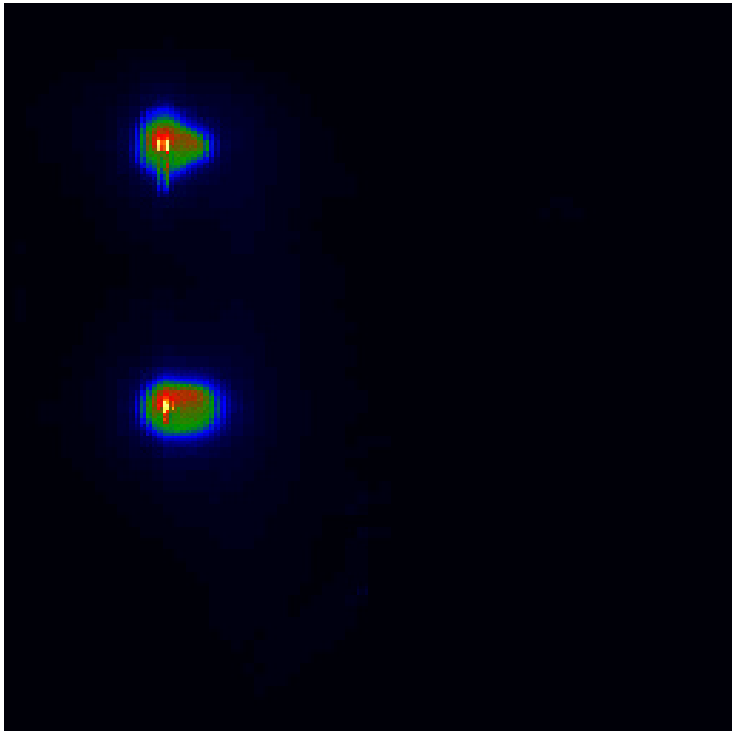
Pulsed Laser Deposition
Plume Evolution

ICCD Images of Dual PLD Plume Evolution



Visible Light



UV Light

0.5 ms exposure, 15 ms total time

Pulsed Laser Deposition
Library Deposition Conditions

	Experiment	Range
Laser Fluence (excimer @ 248 KrF)	~5 J/cm^2	threshold to >100 J/cm^2
Buffer Gas	2.5 Pa O_2	10^{-6} to 40 Pa O_2
Substrate Temperature	600ºC	RT to 800 ºC
Material System	$BaTiO_3$ - $SrTiO_3$	infinite
Targets	pure BT, ST ~ 26 mm centers	
Time	60 minutes / 10 Hz	
Deposition rate	300 to 500 nm/h	

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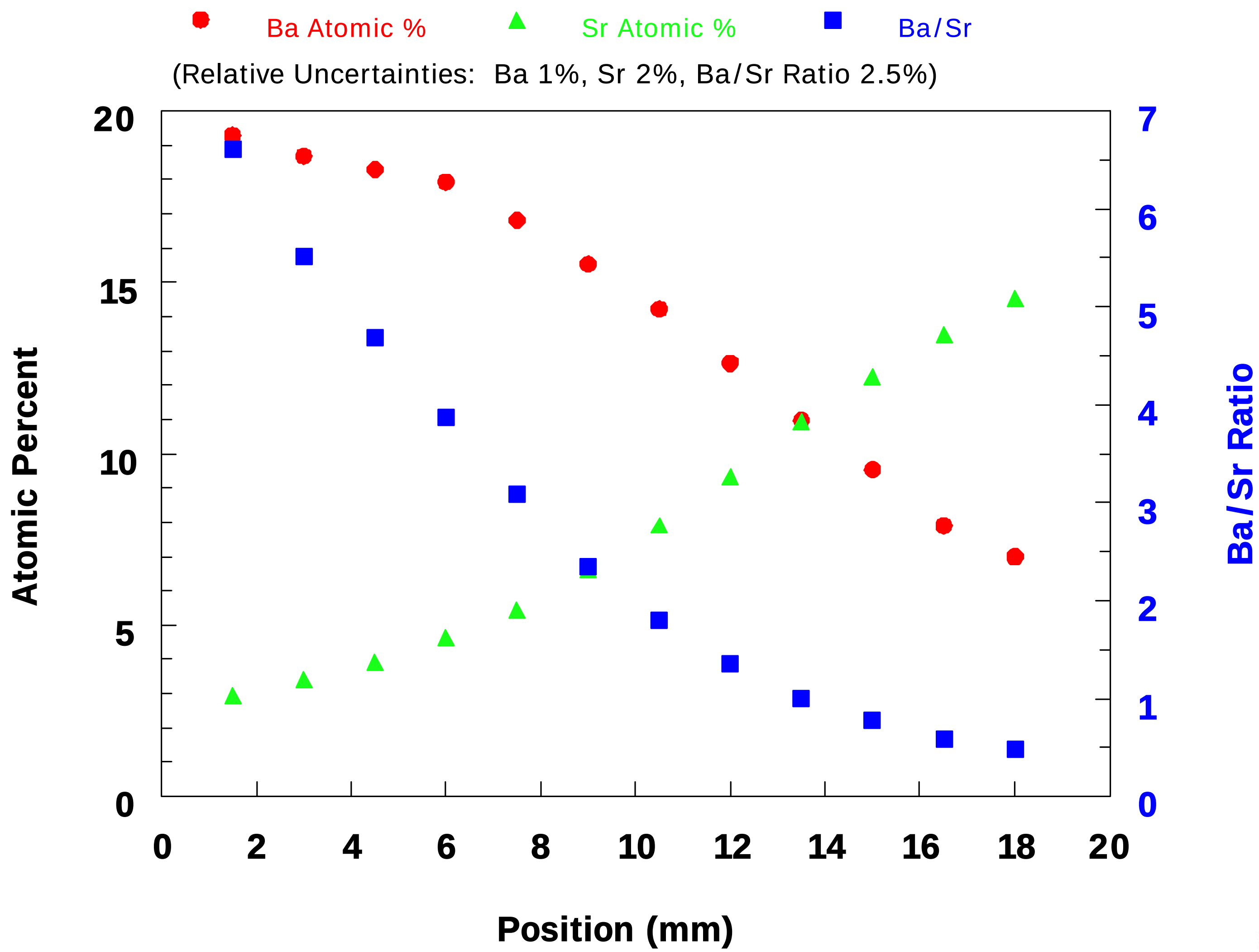
Composition Assay: BT-ST library

EMPA / WDS measurements



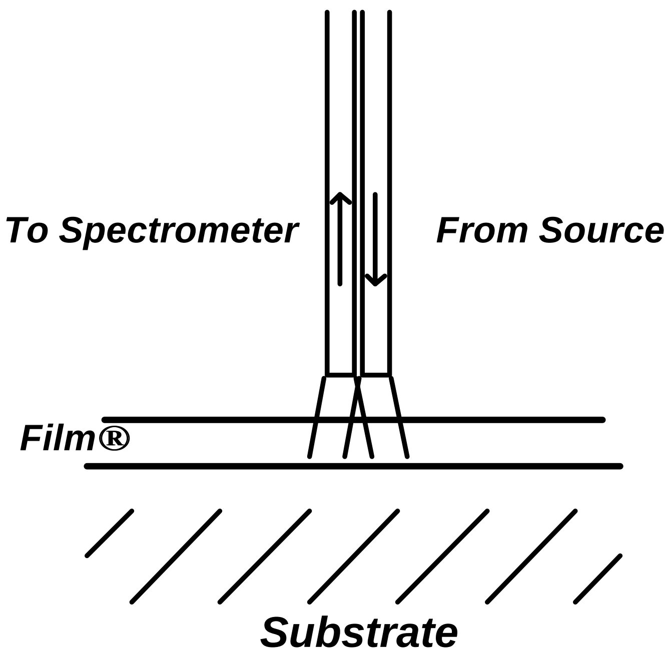
High Throughput Assays
Thickness and Refractive Index

- **Film thickness**
  - **Key parameter in property measurements**
  - **Thickness may not be uniform in a library film – mapping is needed**

- **Refractive index, n**
  - **Measure of light propagation in a material**
  - **Speed of light in vacuum/speed of light in material**
  - **Critical property for optical and transparent conducting materials**

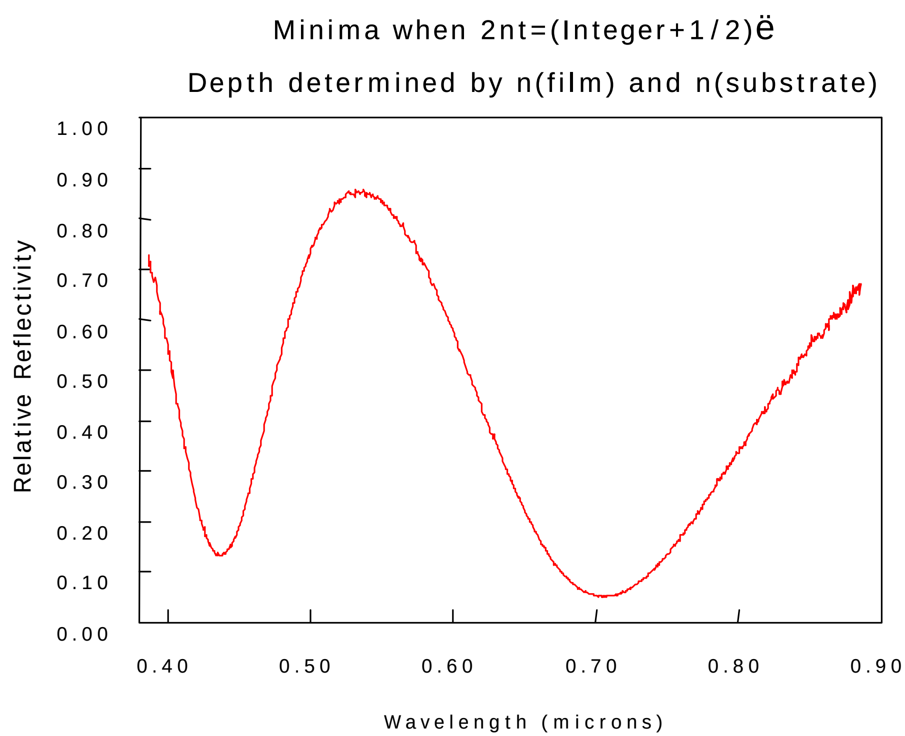
Thickness Mapping
Spectroscopic Reflectometry

Bifurcated Fiber Optic Probe



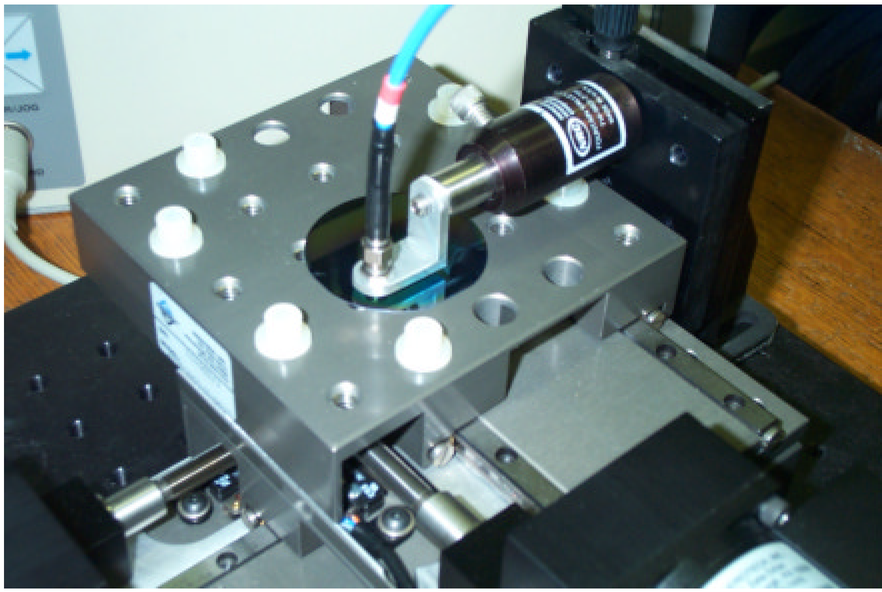
Spatial resolution: 0.5 mm

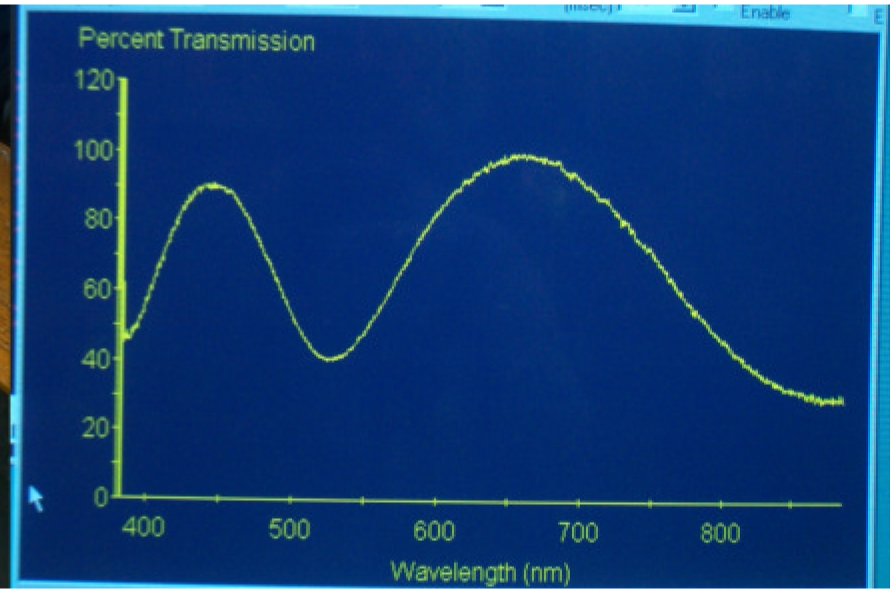
Film Thickness (t) and Index (n)



Spectrum from 317 nm BST film on a silicon substrate

Thickness Mapping
Spatially-resolved Spectroscopic Reflectometry



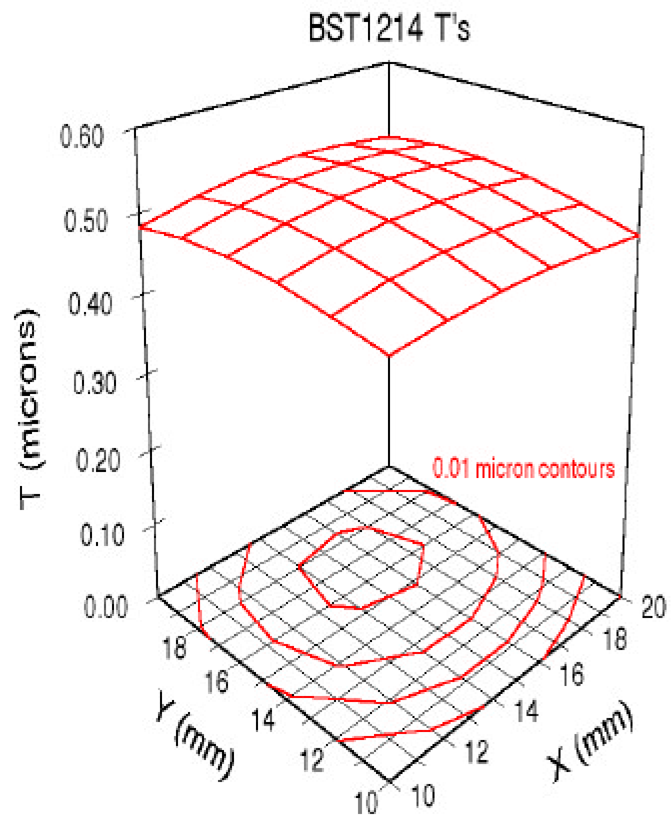


Fully automated mapping of thickness: ~5 s/point

(1-2 s spectrum, 3-4 s for fit)

Thickness Mapping
Uniform thickness films

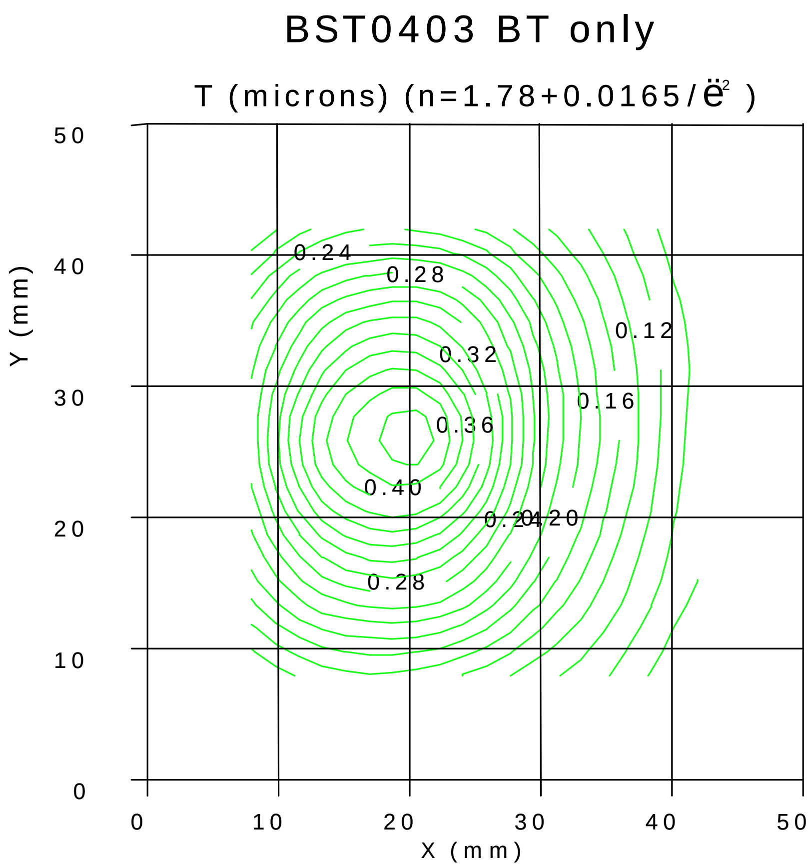
- **Uniform thickness films can simplify analysis of property measurements**
- **Laser plumes were fine-tuned using the *in situ* diagnostics**
- **Thickness uniformity of ~3% over a 1 cm x 1 cm area was achieved**

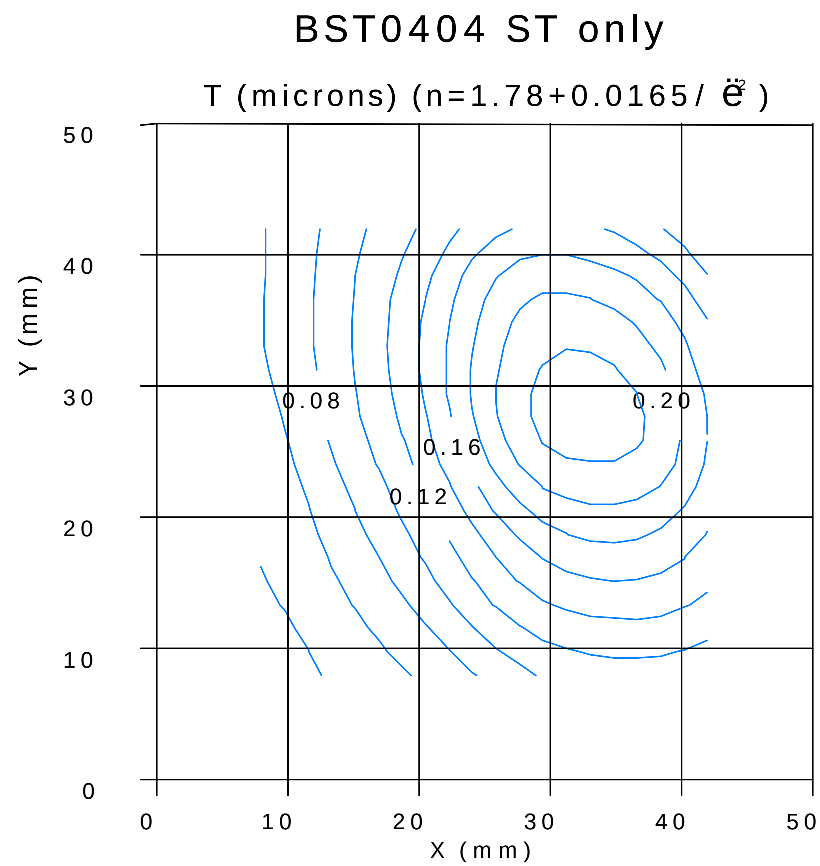


Thickness map of a BT-ST library film

Predicting Composition Maps
Measuring the Deposition Pattern

Deposition Patterns from Individual Targets





Thickness contours from BT target only

Thickness contours from ST target only

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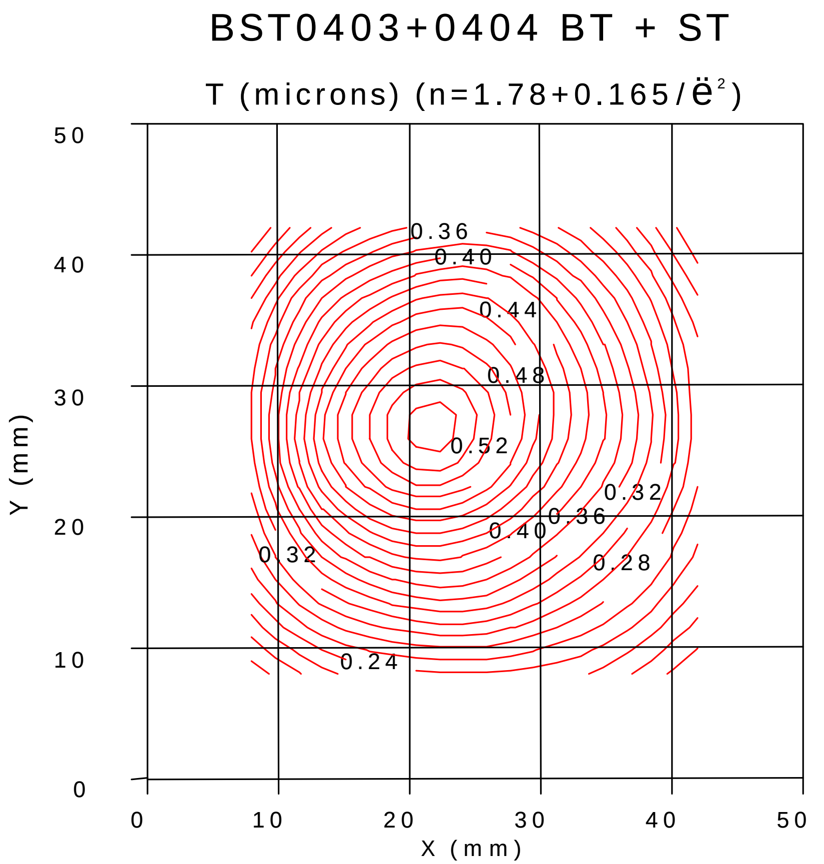
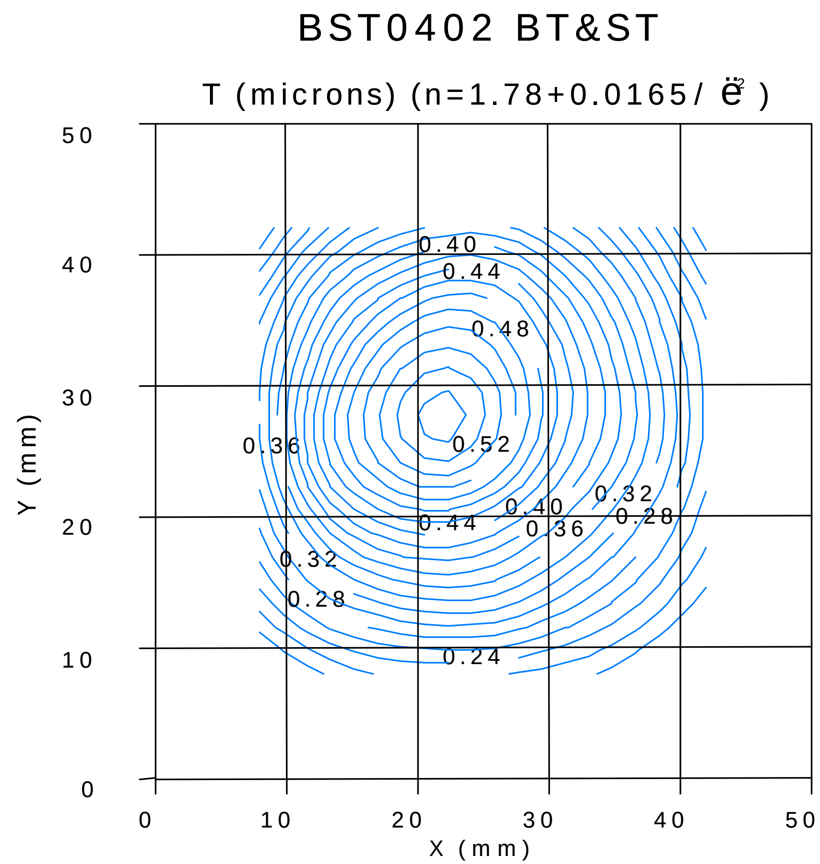
Predicting Composition Maps
Comparing Deposition Patterns



Thickness contours obtained by summing contours for films deposited from individual targets



Thickness contours for a film deposited from both targets

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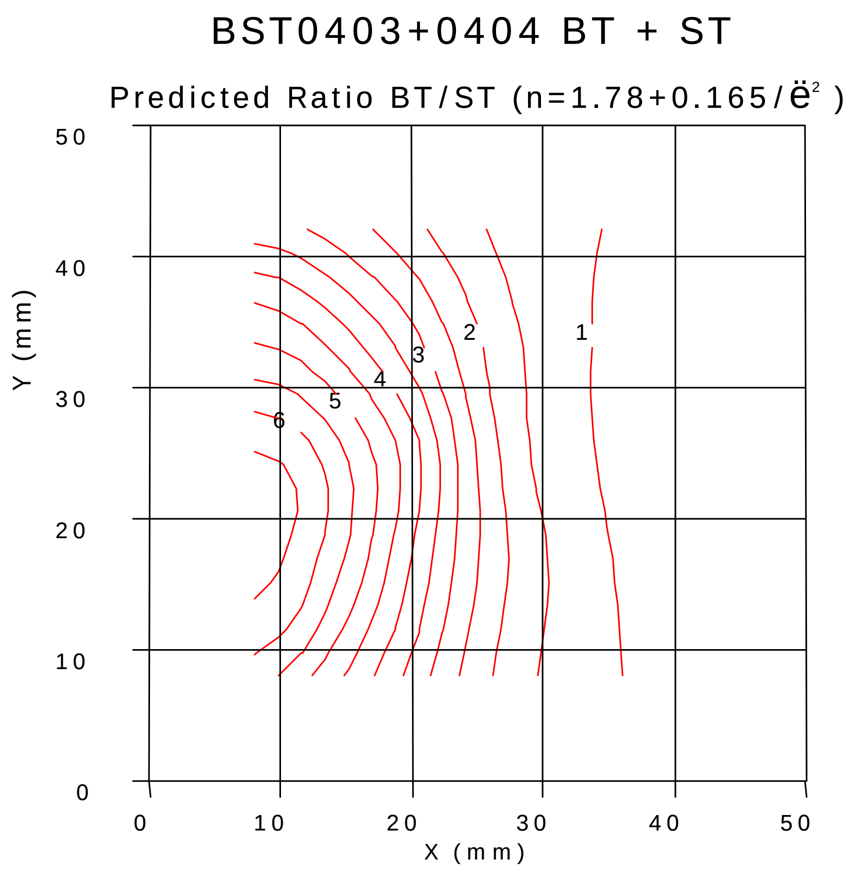
Predicting Composition Maps
From Thickness Maps

- **Excellent correlation of deposition pattern from both targets with pattern obtained by summing individual target patterns**
- **Assume negligible diffusion**
- **Predict composition map from individual target patterns**



Predicted composition ratio Ba/Sr contours

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Phase Evolution Measurements

Tools Under Development

Objective:

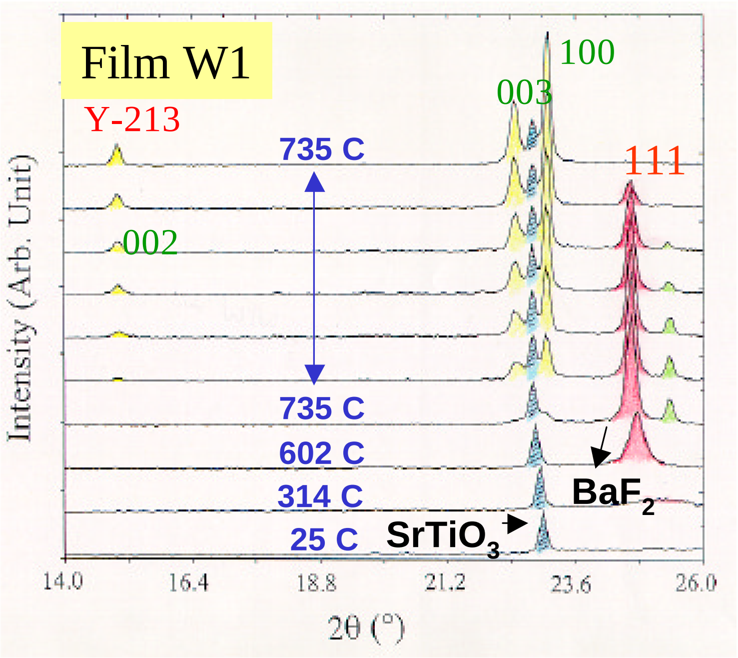
Develop high throughput methodologies to measure phase evolution in thin films as a function of temperature, atmosphere & time

Approach:

- **High temperature XRD:** ***modify existing system to increase measurement rate***
- **Spectroscopic reflectometry:** ***detect phase changes via changes in refractive index***

Status:

- **Demonstrated feasibility of using HTXRD to monitor phase changes in films**
- **Preliminary results on crystallization of ZrO_2 films by XRD and optical methods**



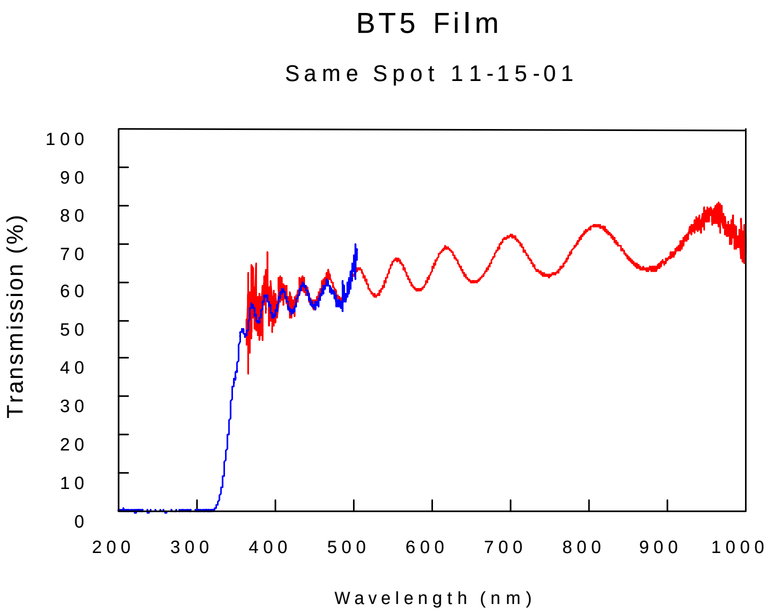
HTXRD results on a 1 ìm Y-Ba-Cu-O-F film on a $SrTiO_3$ substrate

Future work:

- **Establish high throughput measurement protocol for films**

Future Direction
Spectroscopic Reflectometry

- **Expand measurements into the near UV to 200nm**
  - **New UV source, spectrometer, fiber optic probe**
  - **More complex data analysis, models for n and k**
- **Include transmission measurement capability**



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Future Direction

Gold-Nickel Oxide Library Films

- Au-NiO films: transparent electrodes for III-nitride devices
- Informal project with GE's CRD Lab
- Two approaches, both dual target:
    - Au and NiO deposited on heated substrate with O_2
    - Au and Ni deposited, then annealed in air
- Measure optical transmission and electrical conductivity

Summary

Combinatorial tools broadly applicable to inorganic films:

- ***Dual-beam, dual target pulsed laser deposition system for library fabrication***
- ***Spatially-resolved spectroscopic reflectometry technique for high throughput thickness and refractive index mapping***

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NIST Collaborators

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Library fabrication, high-throughput thickness assays

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Composition measurements

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Phase evolution measurements

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